XIII. COMPOUND QUANTITATION AND REPORTED QUANTITATION LIMITS

A. OBJECTIVE

The objective for the evaluation of compound quantitation and reported quantitation limits is to ensure that reported quantitative results and quantitation limits are accurate. To this end, laboratory calculations from raw data to the final reported concentrations are checked for accuracy.

B. CRITERIA

The Region I, EPA-NE Data Validation Functional Guidelines for Evaluating Environmental Analyses should be used to validate all Region I Organic data. The CLP-Volatile/Semivolatile method QC acceptance criteria listed in Appendices A and B should be used as the default criteria when none exist for the Volatile/Semivolatile analytical method utilized and when similar QC parameters are required by the non-CLP method and acceptance criteria have not been specified. Deviations, modifications or non-CLP method-specific QC acceptance criteria may be used but must be explicitly defined in tabular format in the site specific EPA approved QAPjP/SAP or amendment to the QAPjP/SAP.

1. Reported quantitation limits must meet project-required DQOs.

2. a. Reported concentrations for positive detects and compound quantitation limits for non-detects and adjustments of those concentrations/compound quantitation limits must be calculated according to the appropriate method requirements.

   b. Reported concentrations for positive detects and compound quantitation limits for non-detects must be adjusted for percent solids, dilutions, concentrations and cleanup procedures that are not accounted for in the method.

3. a. Target compound quantitation must be based on the internal standard (IS) specified in the method.

   b. Target compound quantitation must be based on the quantitation ion (m/z) specified in the method for both the IS and target compound.

   c. Target compound quantitation must be calculated using the RRF from the appropriate daily standard.

4. Target compound quantitation must be within the initial calibration range.

5. All soil/sediment/solid sample results must be adjusted for percent solids, and must have percent solids greater than 30 percent. [1]

   Sediment samples are collected at CERCLA sites to establish whether or not the presence of hazardous chemicals has impacted

the resident organisms and their natural environment. The data quality objectives for ecological risk assessment generally require that the analytical method used for sediment analysis achieve, at a minimum, the dry weight CLP SOW quantitation limits.

[1]U.S. EPA Office of Water Regulations and Standards Industrial Technology Division - Method 1620, p. 29, Section 14.16, Draft September 1989.

Most analytical methods that deal with soil-type matrices are applicable to both soils and sediments with no difference in how those two matrices are prepared and analyzed. Since a definition for soil and sediment matrices is not provided in the analytical methodology, Region I has adopted the definition for soil samples used by the Office of Water Regulations and Standards Industrial Technology Division (ITD). This definition states that soil samples are "soils, sediments, and sludge samples containing more than 30% solids".

High moisture sediments cannot be successfully analyzed by routine CLP analytical methods. Additional sampling and analytical preparation steps, which are outside of the scope of a CLP method, should be employed. For example, standing water may first be decanted, and then the sample may be centrifuged or filtered to remove excess water (except in the case of samples to be analyzed for volatile organics). To achieve the dry weight quantitation limits, the laboratory must perform a percent solids analysis prior to extraction and the initial volume of sample extracted must be increased accordingly. This presumes that the samplers have collected sufficient volume, above and beyond normal volume requirements, so that additional sample can be extracted. As a last resort, the laboratory can decrease the final extract volume to a minimum of 0.5 milliliters.

Certain solid matrices, such as peat, are unusual in both their reactive chemistry as well as their associated data quality objectives. Peat is a natural sink for organic compounds. It is composed of both a solid spongy matrix (which tightly binds organic compounds) and the interstitial pore water present therein.

Routine analytical methods underestimate the concentrations of organic compounds in peat matrices because the typical organic preparation and extraction techniques do not breach the matrix. In order for peat to be successfully analyzed, the matrix itself must be "sheared" into small pieces to increase surface area so that the extraction solvent can interact to partition the target organic compounds.

Sampling and analytical methodologies must be determined during project scoping processes and must be based on the project data quality objectives. For more information, see Attachment A of the Data Validation Manual.

C. EVALUATION/ D. ACTION

C. EVALUATION	D. ACTION
1. Verify that the reported quantitation limits meet project-required DQOs.	All potential impacts on the sample data resulting from compound quantitation anomalies should be noted in the Data Validation Memorandum. The validator should also document and justify all technical decisions made based on professional judgment in the Data Validation Memorandum. 1. If reported quantitation limits do not meet the project-required DQOs, then the validator must investigate and document the cause of the deficiency and use professional judgment to assess sample data.

C. EVALUATION	D. ACTION
*2. a. Recalculate, from the raw data, the concentrations for at least one positive detect and one sample quantitation limit (for a diluted sample or a soil sample) for each fraction, in every field sample to verify that laboratory reported sample results were accurately calculated according to the method.	2. a. If incorrect values, equations or factors have been used to calculate sample results and/or sample quantitation limits, then the validator should have the laboratory requantitate and resubmit all corrected raw data and forms. If a discrepancy remains unresolved, the validator must use professional judgment to decide which value is accurate. Under these circumstances, the validator may determine that the sample data should be qualified or rejected. A discussion of the rationale for data qualification and the qualifiers used should be documented in the Data Validation Memorandum.

C. EVALUATION	D. ACTION
*2. b. Verify that the concentrations for positive detects and sample quantitation limits have been adjusted to reflect sample dilutions, concentrations, cleanup methods and dry weight factors that are not accounted for in the method.	2. b. If the concentrations for positive detects and/or sample quantitation limits were not correctly adjusted for sample dilutions, concentrations, cleanup methods, or dry weight factors, then the validator should have the laboratory requantitate and resubmit all corrected raw data and forms. If a discrepancy remains unresolved, the validator must use professional judgment to decide which value is accurate. Under these circumstances, the validator may determine that the sample data should be qualified or rejected. A discussion of the rationale for data qualification and the qualifiers used should be documented in the Data Validation Memorandum.
*3. Verify that the correct internal standard, quantitation ion and standard RRF were used to quantitate sample results for at least one positive detect in each fraction in every field sample.	3. If the laboratory utilized an incorrect IS, quantitation ion, or RRF to quantitate a target compound, then the validator should have the laboratory requantitate and resubmit all corrected raw data and forms. If a discrepancy remains unresolved, the validator must use professional judgment to decide which value is accurate. Under these circumstances, the validator may determine that the data should be qualified or rejected. A discussion of the rationale for data qualification and the qualifiers used should be documented in the Data Validation Memorandum.

C. EVALUATION	D. ACTION
4. Verify that the concentrations for positive detects are within the initial calibration range.	4. a. If the concentrations for positive detects exceed the upper limit of the initial calibration range and no dilutions were reported, then the validator should estimate (J) those positive detects that exceed the initial calibration range. b. If the concentrations for positive detects fall below the lower limit of the initial calibration range, then the validator should estimate (J) those positive detects.
5. Ascertain if any soil/sediment/solid sample has less than or equal to 30 percent solids.	5. a. If a soil/sediment/solid sample has greater than 30 percent solids, then the validator should accept all sample data. b. If a soil/sediment/solid sample has percent solids of greater than or equal to 10% but less than or equal to 30%, then the validator should: ! Estimate (J) positive detects. ! Reject (R) non-detects. c. If a soil/sediment/solid sample has less than 10 percent solids, then the validator should reject (R) positive and non-detect sample results as unusable. d. The validator should include a discussion of the sample matrices having low percent solids in the Data Validation Memorandum. The validator may need to contact the field sampler to determine whether sampling techniques were appropriate for the sample matrix.

Note: The following subsections are applicable only to a Tier III data validation:
C.2.a, C.2.b, C.3

Table VOA/SV-XIII-1:

QUALIFICATION OF VOLATILE/SEMIVOLATILE ORGANIC ANALYTES BASED ON SAMPLE PERCENT SOLIDS

Sample Result	% Solids > 30%	10% # % Solids # 30%	% Solids < 10%
Detects	A	J	R
Non-detects	A	R	R

E. EXAMPLES

Example #1: (10% # % Solids # 30%)

DQOs for the Oak Street site specify that soil samples be analyzed for low level PAHs and other semivolatile compounds to assess human health risk posed by the site contamination. Semivolatile soil sample SAA58 had 15% solids and positive detects for chrysene, naphthalene, and benzo(a)pyrene. Due to the low percent solids, the chrysene, naphthalene, and benzo(a)pyrene detects are estimated (J) and all semivolatile non-detects are rejected (R) as unusable because the elevated sample quantitation limits do not meet project DQOs. The validator reports the qualified data on the Data Summary Table and notes this problem in the Data Validation Memorandum.

Example #2: (% Solids < 10%)

Volatile sediment sample SAA89 had 8% solids and positive detects for chlorobenzene, benzene, and trichloroethene. As a result of the extremely low percent solids (< 10%), the validator rejects (R) as unusable all positive detects and non-detects for this sample. The validator contacts the field sampler to determine if sampling techniques were inappropriate for the sample matrix resulting in high moisture content. The validator reports the qualified data on the Data Summary Table and discusses the high moisture content of the sample and the inappropriateness of the sampling and/or analytical methods in the Data Validation Memorandum.

XIV. TENTATIVELY IDENTIFIED COMPOUNDS

A. OBJECTIVE

Chromatographic peaks that are not target analytes, surrogate compounds, or internal standards are potential tentatively identified compounds (TICs). TICs must be qualitatively identified by a mass spectral library search, followed with interpretation by the laboratory's mass spectral interpretation specialist for potential compound identification. Laboratory-reported TICs are also assessed by the data validator.

B. CRITERIA

The Region I, EPA-NE Data Validation Functional Guidelines for Evaluating Environmental Analyses should be used to validate all Region I Organic data. The CLP-Volatile/Semivolatile method QC acceptance criteria listed in Appendices A and B should be used as the default criteria when none exist for the Volatile/Semivolatile analytical method utilized and when similar QC parameters are required by the non-CLP method and acceptance criteria have not been specified. Deviations, modifications or non-CLP method-specific QC acceptance criteria may be used but must be explicitly defined in tabular format in the site specific EPA approved QAPjP/SAP or amendment to the QAPjP/SAP.

1. In accordance with the method, the laboratory must conduct mass spectral library searches for each sample and blank to report the possible identity of a specified number of volatile and semivolatile chromatographic peaks which are not surrogate compounds, internal standards, or target compounds, but which have an area count or peak height greater than 10 percent of the area count or peak height of the nearest internal standard. All GC/MS library searched mass spectra for every sample and blank must be examined by the laboratory for tentative compound identification.

   NOTE: The laboratory should not report, as a tentatively identified compound, any target compound which is properly reported in another fraction. For example, late eluting volatile target compounds should not be reported as semivolatile TICs.

2. TIC concentrations should be qualified by the laboratory as estimated (J). TIC concentrations should be calculated by the laboratory assuming an RRF of 1.0 and using the closest eluting IS that is free of interferences.

3. Chromatograms for blanks should not contain any TIC peaks.

4. Guidelines for making tentative identifications are as follows:

   a. Major ions (greater than 10 percent relative intensity) in the reference spectrum should be present in the sample spectrum.

   b. The relative intensities of the major ions should agree within ± 20 percent between the sample and reference spectra.

   c. Molecular ions present in the reference spectrum should be present in

the sample spectrum.

4. d. Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination, interference, or coelution of additional TIC or target compound(s).

   e. Since library searches often yield several candidate compounds having closely matching scores, all reasonable choices must be considered and the most reasonable candidate chosen.

   f. When the above criteria are not met, but in the technical judgment of the validator or mass spectral interpretation specialist the identification is correct, the validator may report the identification.

   g. If in the validator's judgment the identification is uncertain or there are extenuating factors affecting compound identifications, the TIC result may be reported as "unknown".

5. The following common laboratory artifacts/contaminants and their sources (e.g., aldol condensation products, solvent preservatives, and reagent contaminants) should not be reported as TICs.

   Examples:

   a. Common laboratory contaminants: CO_2 (m/z 44), siloxanes (m/z 73), diethyl ether, hexane, certain freons (1,1,2-trichloro-1,2,2-trifluoroethane or fluoro-trichloromethane), and phthalates at levels less than 100 ug/L or 4000 ug/Kg.

   b. Solvent preservatives such as cyclohexene - a methylene chloride preservative. Related by-products include cyclohexanone, cyclo-hexenone, cyclohexanol, cyclohexenol, chlorocyclohexene, and chlorocyclohexanol.

   c. Aldol condensation reaction products include: 4-hydroxy-4-methyl-2-pentanone, 4-methyl-2-penten-2-one, and 5,5-dimethyl-2(5H)-furanone.

C. EVALUATION/ D. ACTION

C. EVALUATION	D. ACTION
	All potential impacts on the sample data resulting from tentatively identified compound anomalies should be noted in the Data Validation Memorandum. The validator should also document and justify all technical decisions made based on professional judgment in the Data Validation Memorandum.
* 1. a. Verify that the laboratory has generated a library search for all required peaks in the sample and blank chromatograms.	1. a. If the laboratory has neglected to generate a library search for all required peaks, then the validator should have the laboratory requantitate and resubmit all corrected raw data and forms should be resubmitted. If a discrepancy remains unresolved, the validator must use professional judgment to decide which identification is accurate. Under these circumstances, the validator may determine that the sample data should be qualified or rejected. A discussion of the rationale for data qualification and the qualifiers used should be documented in the Data Validation Memorandum.
b. Verify that reported TIC peaks were not surrogate compounds or internal standards.	b. If the laboratory performed a library search on a surrogate compound or internal standard, the validator should not report that compound as a TIC on the Tentatively Identified Compounds Table-Table III.

C. EVALUATION	D. ACTION
c. Verify that a target compound from another organic fraction was not reported as a TIC.	c. If the laboratory reported a target compound from another organic fraction as a TIC, then the validator should check that fraction to determine if the laboratory correctly identified the target compound in that organic fraction. If the laboratory did not correctly identify the target compound in that fraction, then the laboratory should be contacted to requantitate the false negative result, report that compound with the proper fraction, and remove that compound from the TIC form.
*1. d. Verify that a target compound was not missed by the target compound search procedure and erroneously reported as a TIC in the proper analytical fraction. The validator should evaluate other sample chromatograms and check library reference retention times on quantitation lists to determine whether the false negative result is an isolated occurrence or whether data from the entire case may be affected.	1. d. If the laboratory reported a target compound from the proper fraction as a TIC, then the validator should contact the laboratory to requantitate the false negative result, report that compound on the correct form, and remove that compound from the TIC form.

C. EVALUATION	D. ACTION
*2. Verify that all TICs are reported with estimated (J) concentrations by the laboratory. Verify that TIC concentrations were calculated correctly, assuming a RRF of 1.0 and using the closest eluting IS that is free of interferences.	2. Qualify all TIC concentrations as estimated (J) if the laboratory has not already done so. If the laboratory did not quantitate the TIC assuming an RRF of 1.0 and using the appropriate IS, then the validator should have the laboratory requantitate and resubmit all corrected raw data and forms. If a discrepancy remains unresolved, the validator must use professional judgment to decide which value is accurate. Under these circumstances, the validator may determine that the sample data should be qualified or rejected. A discussion of the rationale for data qualification and the qualifiers used should be documented in the Data Validation Memorandum.
*3. Verify that the blanks do not contain any TIC peaks. When a low level non-target compound is detected in a sample, a thorough check of blank chromatograms may be required. Look for peaks which are less than 10% of the area/height of the nearest, interference-free IS, and which are present in the blank chromatogram at a similar relative retention time.	3. a. If any TIC is found in a sample at a concentration greater than 10 times the level detected in an associated blank, then the TIC should be reported. b. If any TIC is found in a sample at a concentration less than or equal to 10 times the level detected in an associated blank, then the TIC should not be reported.

C. EVALUATION	D. ACTION
*4. a. Examine all TIC mass spectra in every sample and blank. Compare sample TIC spectra with all library search spectra to confirm that the most reasonable candidate was chosen according to the criteria set forth in Section XIV, B.4.	4. a. The validator must use professional judgment to determine if the criteria in Section XIV, B.4 were met and a reasonable identification was made. If there is more than one possible match, then the result may be reported as "either compound X or compound Y". If there is a lack of isomer specificity, the TIC result may be changed to a non-specific isomer result (e.g., 1,3,5-trimethyl benzene to trimethyl benzene isomer) or to a compound class (e.g., 2-methyl, 3-ethyl benzene to substituted aromatic compound). The validator may elect to quantitatively report all similar isomers as the sum of the individual isomers. For example, all alkanes may be quantitatively summed and reported as total hydrocarbons. The validator must summarize any changes made to the laboratory data and must document the rationale used to justify those changes in the Data Validation Memorandum.
* b. Verify that TICs were reported as unknowns if the TIC spectra presented do not meet the criteria set forth in Section XIV, B.4 and thus no reasonable choices could be determined.	b. If it is determined that a tentative identification of a non-TCL compound is unacceptable, then the tentative identification should be changed to unknown or to an appropriate identification. c. Other case factors may influence TIC judgments. If a sample TIC match is poor but other samples have a TIC with a good library match, similar relative retention time, and the same ions, then identification information may be inferred from the other sample TIC results.

C. EVALUATION	D. ACTION
* 5. Review blank and sample TIC spectra to ensure that common laboratory artifacts/contaminants are not reported as TICs. (See Section XIV, B.5 for examples of common laboratory artifacts/contaminants.)	5. If a common laboratory artifact and/or contaminant is reported as a TIC in a blank or sample, then the validator should not report the TIC on Table III TICs.

*** Note: The following subsections are applicable only to a Tier III data validation:**

C.1.a, C.1.d, C.2, C.3, C.4.a, C.4.b, C.5

E. EXAMPLES

Example #1: (Target analyte improperly reported as TIC in another fraction)

The laboratory originally reported 1,2-dichlorobenzene as a TIC in the volatile fraction of soil sample SAA12. 1,2-dichlorobenzene, however, was reported as a non-detect in the semivolatile fraction. Upon review of the semivolatile chromatogram for sample SAA12, the validator notes that the laboratory failed to identify a peak that eluted within the 1,2-dichlorobenzene retention time window. The laboratory was contacted and requested to requantitate the false negative semivolatile 1,2-dichlorobenzene result and report 1,2-dichlorobenzene as a positive detect in the semivolatile fraction, as well as remove the result from the VOA TIC form. The laboratory complied and the validator reports 1,2-dichlorobenzene as a positive detect in the semivolatile fraction on the Data Summary Table.

Example #2: (TIC not reported, lack of spectral confirmation)

Dichloronaphthalene is reported as a TIC in semivolatile sample SAA35. The reference dichloronaphthalene mass spectrum has a molecular ion of 196 and a 198, m+2, ion, with a relative intensity of 66.0%. The sample dichloronaphthalene mass spectrum has a molecular ion of 196 but the 198 ion has a 10.0% relative intensity. Because the sample spectrum's chlorine isotope (m+2 ion) relative intensity is not within ± 20.0% of the reference spectrum's relative intensity, the presence of dichloronaphthalene is not confirmed in the field sample. The validator uses professional judgment to determine that dichloronaphthalene is not present in the field sample, changes the TIC designation to "unknown", and justifies this in the Data Validation Memorandum. The validator does not report that TIC on the "Tentatively Identified Compound-Table III" since "unknowns" are not included on that table.

Example #3: (Unreported peak with relative intensity greater than 10% of the nearest IS)

The validator verifies that all peaks greater than 10% of the nearest IS for sample SAA01 are accounted for in the chromatogram and quantitation report for sample SAA01. To do this, the validator identifies target compound, internal standard, and surrogate peaks on the chromatogram quantitation report, and the Form I. The remaining peaks (greater than 10% of the nearest IS) should be listed as TICs. The validator notes that one peak (greater than 10% of the nearest IS) is unaccounted for and contacts the laboratory to obtain sample and reference mass spectra and to request revision of the Form I TIC. The laboratory complies and the validator reports that TIC on the "Tentatively Identified Compound-Table III" in the Data Validation Memorandum.

XV. SEMIVOLATILE CLEANUP

A. OBJECTIVE

Semivolatile cleanup procedures are utilized to remove matrix interferences from sample extracts prior to analysis. If not removed from the sample extracts, matrix interferences can inhibit accurate compound identification and quantitation resulting in highly suspect data. Semivolatile cleanup procedures are checked by spiking the cleanup columns or cartridges with target compounds, and evaluating the recovery of semivolatiles through the cleanup procedure.

Several types of semivolatile cleanup procedures exist, including but not limited to:

1. **Gel Permeation Chromatography (GPC)** - separates compounds based on molecular size and can be used to remove high molecular weight interferents.

   GPC is a size exclusion procedure that utilizes organic solvents and hydrophobic gels to separate macromolecules. The packing gel is porous and is characterized by the exclusion range (range of uniformity) of that pore size. The exclusion range must be greater than those of the molecules to be separated.

   General applications of GPC as a cleanup procedure for semivolatile organic fractions include the removal of lipids, polymers, copolymers, proteins, natural resins and polymers, cellular components, viruses, steroids and dispersed high molecular-weight compounds from the sample extract.

   Under CLP SOW OLM03.2, the GPC column is packed with bead-like packing and connected to a UV detector. After the GPC is calibrated and a blank analyzed, sample extracts are loaded into sample loops and an automated sequence is started. The target compounds are eluted with methylene chloride and collected during the pre-determined retention times. The high molecular weight interferences, those outside the exclusion range, elute earlier than the TCL semivolatile compounds during the "dump" phase, while the smaller interferents such as sulfur elute with a later volume of solvent during the "wash" phase.

2. **Silica Gel Cleanup** - separates interferents of different polarity.

   Silica gel is a regenerative adsorbent of amorphous silica with weakly acidic properties and is used for separating compounds of differing chemical polarity. Silica gel can be used for the cleanup of sample extracts containing polynuclear aromatic hydrocarbons (PAHs) and derivatized phenolic compounds.

   The silica gel column is packed with the required amounts of adsorbent, topped with a water adsorbent, and then loaded with a sample extract. The analytes are eluted with solvents of increasing polarity, to achieve desired separation, leaving the interfering compounds on the column.

Note: The CLP SOW OLM03.2 semivolatile method uses only GPC cleanup.

B. CRITERIA

The Region I, EPA-NE Data Validation Functional Guidelines for Evaluating Environmental Analyses should be used to validate all Region I Organic data. The CLP-Volatile/Semivolatile method QC acceptance criteria listed in Appendices A and B should be used as the default criteria when none exist for the Volatile/Semivolatile analytical method utilized and when similar QC parameters are required by the non-CLP method and acceptance criteria have not been specified. Deviations, modifications or non-CLP method-specific QC acceptance criteria may be used but must be explicitly defined in tabular format in the site-specific EPA approved QAPjP/SAP or amendment to the QAPjP/SAP.

1. **Gel Permeation Chromatography**

   a. Semivolatile sample extracts, QC sample extracts, and method blank extracts must undergo all cleanup procedures required by the method.

   b. The GPC system must be calibrated initially in accordance with the method prior to the analysis of field samples, QC samples or blanks to ensure acceptable solid phase activation, peak shape, and resolution of target compounds and interferents.

   c. i. GPC calibration must be checked on a continuing basis at the frequency specified in the method.

      ii. The method-required GPC calibration check solution must contain target and surrogate compounds and interferents at the method-required concentrations and must be analyzed according to the analytical method.

      iii. Target compound recoveries must meet method QC acceptance criteria.

      iv. Surrogate compound and internal standard area counts and/or retention times must meet method QC acceptance criteria.

      v. Peak shapes must be symmetrical and resolution must meet method QC acceptance criteria.

      vi. Retention time shifts between GPC calibration checks must not exceed ±5% between calibrations.

   d. i. A GPC instrument blank spiked with surrogate compounds must be analyzed after each GPC calibration and calibration check and prior to sample analysis.

      ii. Target compounds must not be present at greater than or equal to the quantitation limit for any target compound in the GPC

instrument blank.

iii. Surrogate compound recoveries and internal standard area counts and/or retention times (if added) in GPC instrument blanks must meet method QC acceptance criteria after GPC cleanup. Note: CLP SOW OLM03.2 does not require the addition of surrogate compounds or internal standards to the GPC instrument blank.

2. **Silica Gel Cleanup**

a. Semivolatile sample extracts, QC sample extracts and method blank extracts must undergo all cleanup procedures required by the method.

b. Each lot number of solid phase adsorbent must be checked in accordance with the method prior to use to ensure acceptable solid phase activation, recovery of target analytes, and elimination of interferents.

c. i. A Silica Gel Check solution must be prepared with each cleanup batch and must be analyzed prior to the Silica Gel column reagent blank. For each batch of samples undergoing Silica Gel column cleanup, the column performance must be checked with a Silica Gel Check solution to demonstrate that the compounds of interest are being quantitatively recovered.

ii. The method-required Silica Gel Check solution must contain target and surrogate compounds and interferents at method-required concentrations and must be prepared and analyzed according to the analytical method.

iii. Target compound recoveries must meet method QC acceptance criteria.

iv. Surrogate compound and internal standard area counts and/or retention times must meet method QC acceptance criteria.

d. i. A Silica Gel column reagent blank spiked with surrogate compounds must be prepared with each cleanup batch. The Silica Gel column reagent blank must be analyzed after the Silica Gel Check solution and prior to field samples.

ii. Target compounds must not be present at greater than or equal to the quantitation limit for any target compound in the Silica Gel column reagent blank.

iii. Surrogate compound recoveries and internal standard area counts and/or retention times (if added) in Silica Gel column reagent blanks must meet method QC acceptance criteria after Silica Gel column cleanup.

C. EVALUATION/ D. ACTION

C. EVALUATION	D. ACTION
1. Gel Permeation Chromatography (GPC)	All potential impacts on the sample data resulting from sample cleanup anomalies should be noted in the Data Validation Memorandum. The validator should also document and justify all technical decisions made based on professional judgment in the Data Validation Memorandum. **1. Gel Permeation Chromatography (GPC)**
a. Verify from result forms, if available, that GPC cleanup was performed according to the analytical method on all method-required sample extracts, QC sample extracts, and method blank extracts.	a. If GPC was not performed according to the analytical method on all method-required extracts, then the raw data should be reviewed for the presence of high molecular weight contaminants and professional judgment should be used to qualify or reject sample data. The validator should request sample cleanup and reanalysis if GPC was required by the method.
* b. Verify that the GPC system was calibrated initially in accordance with the method requirements and that peak shape and resolution criteria were met.	b. If the GPC system was not calibrated initially in accordance with the method (prior to the analysis of field samples, QC samples or blanks) or fails to meet peak shape and/or resolution criteria or the initial calibration data are not available for review, then the validator should evaluate the last calibration check analyzed just prior to sample analysis.
* c. i. Confirm from the raw data that the GPC calibration check was performed at the method-required frequency.	c. i. If GPC calibration checks have not been performed at the method-required frequency, then the quality of the GPC operation may be suspect and the validator should use professional judgment to qualify or reject sample data.
* ii. Verify that a GPC calibration check solution was analyzed in accordance with the method and that the correct target and surrogate compounds, interferents and concentrations were used.	ii. If a GPC calibration check solution was not analyzed in accordance with the method or the correct compounds and/or concentrations were not used, then the data quality may be adversely affected. In these circumstances, the validator should use professional judgment to qualify or reject sample data.

C. EVALUATION	D. ACTION
1. c. iii. Check the reported data from the GPC calibration check solution analyses to verify that target compound recoveries meet method QC acceptance criteria.	1. c. iii. If GPC calibration check method QC acceptance criteria are not met, then the GPC calibration check solution results should be used to qualify sample data for specific compounds included in the check solution. Professional judgment should be used to qualify or reject sample data for non-check solution compounds, taking into consideration the compound's chemical class. The validator should discuss the impact of unacceptable recoveries on the sample data in terms of high or low bias and note this in the Data Validation Memorandum. If a GPC calibration check compound recovery is greater than the upper limit of the method QC acceptance criteria, then the validator should: - Estimate (J) the affected compound when detected in any sample associated with that GPC calibration check to indicate potential high bias. - Accept the quantitation limit of the affected compound in any sample associated with that GPC calibration check. If more than half of the GPC calibration check compound recoveries are greater than the upper limit of the method QC acceptance criteria, then the validator should: - Estimate (J) all positive detects in all samples associated with that GPC calibration check to indicate potential high bias. - Accept all quantitation limits for non-detects in all samples associated with that GPC calibration check. If a GPC calibration check compound recovery is less than the lower limit of the

C. EVALUATION	D. ACTION
1. c. Continued from above.	1. c. iii. Continued from above. If more than half of the GPC calibration check compound recoveries are less than the lower limit of the method QC acceptance criteria but greater than or equal to 10%, then the validator should: - Estimate (J) all positive detects in all samples associated with that GPC calibration check to indicate potential low bias. - Estimate (UJ) all quantitation limits for non-detects in all samples associated with that GPC calibration check to indicate potential low bias. If a GPC calibration check compound recovery is less than 10%, then the validator should: - Estimate (J) the affected compound when detected in any sample associated with that GPC calibration check to indicate potential low bias. - Reject (R) the quantitation limit of the affected compound in any sample associated with that GPC calibration check to indicate that the data are unusable due to the possibility of false negatives. If more than half of the GPC calibration check compound recoveries are less than 10%, then the validator should: - Estimate (J) all positive detects in all samples associated with that GPC calibration check to indicate potential low bias. - Reject (R) the quantitation limits for all non-detects in all samples associated with that GPC calibration check to indicate that the data are unusable due to the possibility of false negatives. If more than half of the GPC calibration check

C. EVALUATION	D. ACTION
*1. c. iv. Verify that surrogate compound recoveries and internal standard area counts and/or retention times in the GPC calibration check meet method QC acceptance criteria.	1. c. iv. If surrogate compound recoveries and/or internal standard area counts or retention times in the GPC calibration check do not meet method QC acceptance criteria, then the validator should qualify the sample data in accordance with Sections VI and VII.
* v. Review the raw GPC calibration check data to verify that peaks are symmetrical and resolution meets method QC acceptance criteria for target and surrogate compounds and interferents in the GPC calibration check solution.	v. If the GPC calibration check method QC acceptance criteria do not meet peak shape and compound resolution, then the raw sample data should be examined for the presence of high molecular-weight interferences or the loss of late eluting target compounds and professional judgment should be used to qualify or reject sample data. The validator should discuss the impact of unacceptable peak shape and resolution on the sample data in terms of high or low bias and/or the possibility of false negatives and note this in the Data Validation Memorandum.
* vi. Check the raw GPC calibration check data to verify that retention times for any compounds or interferents in the GPC calibration solution did not vary more than ± 5% between calibrations.	vi. Retention time shifts indicate instrument performance problems that require laboratory corrective actions. If retention time shifts are excessive, the GPC cleanup procedure may be the cause of analyte losses and false negatives, and the validator should evaluate the sample data carefully and document all deficiencies in the Data Validation Memorandum.
* d. i. Verify that a GPC instrument blank was analyzed after each GPC calibration and calibration check and prior to sample analysis.	d. i. If a GPC instrument blank was not analyzed at the correct frequency and in the proper sequence, then the validator must use professional judgment in conjunction with the blank guidance provided in Section V to qualify or reject sample data.
* ii. Verify that there are no target compounds present at greater than or equal to the quantitation limit in the GPC instrument blank.	ii. If any target compounds are detected in the GPC instrument blank at greater than or equal to the quantitation limit, then the quality of the GPC operation is
* iii. Verify that surrogate compound recoveries and internal standard area counts and/or retention times (if added) in the GPC instrument blank meet method QC acceptance criteria.	

C. EVALUATION	D. ACTION
*1. e. Compare the raw data to the reported results, if available, and verify that no calculation and/or transcription errors have occurred. If result forms are not available, then the validator must review the cleanup logs to confirm that method required cleanups were performed.	1. e. If the laboratory made any calculation and/or transcription errors, the validator should have the laboratory requantitate and resubmit all corrected raw data and forms. If a discrepancy remains unresolved, the validator must use professional judgment to decide which value is most accurate. Under these circumstances, the validator may determine that the sample data should be qualified or rejected. A discussion of the rationale for data qualification and the qualifiers used should be documented in the Data Validation Memorandum.
f. Review MS/MSD, surrogate, and PES data to evaluate the efficiency of the GPC cleanup.	f. If any compound or compound class has zero recovery indicating the possibility of false negatives and/or recovers low indicating a potential low bias, then the validator should discuss the possible false negatives and/or potential low bias in the Data Validation Memorandum and qualify and/or reject sample results according to the guidance provided in Sections VI, VIII and XI.

C. EVALUATION	D. ACTION
2. Silica Gel Cleanup	**2. Silica Gel Cleanup**
a. Verify from result forms, if available, that Silica Gel cleanup was performed according to the analytical method on all method-required sample extracts, QC sample extracts, and method blank extracts.	a. If Silica Gel cleanup was not performed according to the analytical method on all method-required extracts, then the data should be reviewed for the presence of interferents and professional judgment should be used to qualify or reject sample data. The validator should request sample cleanup and reanalysis if Silica Gel cleanup was required by the method.
b. Verify that each lot of Silica Gel used to cleanup samples was checked prior to use in accordance with method requirements.	b. If each lot of Silica Gel was not checked, then the solid phase may not be properly activated potentially resulting in unacceptable target compound recoveries, the presence of interferents and possibly the loss of target compounds (false negatives). The validator should review the Silica Gel Check solution data associated with each batch of Silica Gel column cleanups to ascertain if any target compounds should be qualified or rejected using the guidance provided in Section XV, D.2.c.iii.
c. i. Verify from result forms, if available, that a Silica Gel Check solution was prepared with each batch of samples undergoing Silica Gel cleanup and analyzed prior to the Silica Gel column reagent blank in accordance with the analytical method.	c. i. If the laboratory did not prepare and analyze the Silica Gel check solution at the correct frequency and sequence, according to the method, then the validator should use professional judgment to qualify or reject sample data.

C. EVALUATION	D. ACTION
*2. c. ii. Verify that a Silica Gel Check solution was prepared and analyzed in accordance with the method and that the correct target and surrogate compounds, interferents and concentrations were used.	2. c. ii. If a Silica Gel Check solution was not prepared and analyzed in accordance with the method or the correct compounds and/or concentrations were not used, then the data quality may be adversely affected. In these circumstances, the validator should use professional judgment to qualify or reject sample data.
iii. Check the reported data from the Silica Gel Check solution analyses to verify that target compound recoveries meet method QC acceptance criteria.	iii. If Silica Gel cleanup method QC acceptance criteria are not met, then the Silica Gel Check solution results should be used to qualify sample data for specific compounds included in the check solution. Professional judgment should be used to qualify or reject sample data for non-check solution compounds, taking into consideration the compound's chemical class. The validator should discuss the impact of unacceptable recoveries on the sample data in terms of high or low bias and note this in the Data Validation Memorandum. If a Silica Gel Check solution compound recovery is greater than the upper limit of the method QC acceptance criteria, then the validator should: - Estimate (J) the affected compound when detected in any sample associated with that Silica Gel Check solution to indicate potential high bias. - Accept the quantitation limit of the affected compound in any sample associated with that Silica Gel Check solution. If more than half of the

C. EVALUATION	D. ACTION
2. c. Continued from above.	2. c. iii. Continued from above If a Silica Gel Check solution compound recovery is less than the lower limit of the method QC acceptance criteria but greater than or equal to 10%, then the validator should: - Estimate (J) the affected compound when detected in any sample associated with that Silica Gel Check solution to indicate potential low bias. - Estimate (UJ) the quantitation limit of the affected compound in any sample associated with that Silica Gel Check solution to indicate potential low bias. If more than half of the Silica Gel Check solution compound recoveries are less than the lower limit of the method QC acceptance criteria but greater than or equal to 10%, then the validator should: - Estimate (J) <u>all</u> positive detects in all samples associated with that Silica Gel Check solution to indicate potential low bias. - Estimate (UJ) <u>all</u> quantitation limits for non-detects in all samples associated with that Silica Gel Check solution to indicate potential low bias. If a Silica Gel Check solution compound recovery is less than 10%, then the validator should: - Estimate (J) the affected compound when detected in any sample associated with that Silica Gel Check solution to indicate potential low bias. - Reject (R) the

C. EVALUATION	D. ACTION
2. c. iii. Continued from above.	2. c. iii. Continued from above. If more than half of the Silica Gel Check solution compound recoveries are less than 10%, then the validator should: - Estimate (J) <u>all</u> positive detects in all samples associated with that Silica Gel Check solution to indicate potential low bias. - Reject (R) the quantitation limits for <u>all</u> non-detects in all samples associated with that Silica Gel Check solution to indicate that the data are unusable due to the possibility of false negatives. If more than half of the Silica Gel Check solution compound recoveries are outside the method QC acceptance limits in one Silica Gel Check solution, where some recoveries are low and some recoveries are high, then the validator should use professional judgment to qualify or reject a particular compound, class of compounds or the entire fraction for samples associated with that Silica Gel Check solution.
* iv. Verify that surrogate compound recoveries and internal standard area counts and/or retention times in the Silica Gel Check solution meet method QC acceptance criteria.	iv. If surrogate compound recoveries and/or internal standard area counts or retention times in the Silica Gel Check solution do not meet method QC acceptance criteria, then the validator should qualify the sample data in accordance with Sections VI and VII.
* d. i. Verify that a Silica Gel column reagent blank was prepared with each cleanup batch and was analyzed after the Silica Gel Check solution but prior to field samples.	d. i. If a Silica Gel column reagent blank was not prepared and analyzed at the correct frequency and in the proper sequence, then the validator must use professional judgment in conjunction with the blank
* ii. Verify that there are no target compounds present at greater than or equal to the quantitation limit in the Silica Gel column reagent blank.	

C. EVALUATION	D. ACTION
*2. d. iii. Verify that surrogate compound recoveries and internal standard area counts and/or retention times (if added) in the Silica Gel column reagent blank meet method QC acceptance criteria.	2. d. iii. If surrogate compound recoveries and/or internal standard area counts or retention times in the Silica Gel column reagent blank do not meet method QC acceptance criteria, then the validator should qualify the sample data in accordance with Sections V, VI, and VII.
* e. Compare the raw data to the reported results, if available, and verify that no calculation and/or transcription errors have occurred. If result forms are not available, then the validator must review the cleanup logs to confirm that method required cleanups were performed.	e. If the laboratory made any calculation and/or transcription errors, the validator should have the laboratory requantitate and resubmit all corrected raw data and forms. If a discrepancy remains unresolved, the validator must use professional judgment to decide which value is most accurate. Under these circumstances, the validator may determine that the sample data should be qualified or rejected. A discussion of the rationale for data qualification and the qualifiers used should be documented in the Data Validation Memorandum.
f. Review MS/MSD, surrogate, and PES data to evaluate the efficiency of the Silica Gel cleanup.	f. If any compound or compound class has zero recovery indicating the possibility of false negatives and/or recovers low indicating a potential low bias, then the validator should discuss the possible false negatives and/or potential low bias in the Data Validation Memorandum and qualify and/or reject sample results according to the guidance provided Sections VI, VIII and XI.

*** Note: The following subsections are applicable only to a Tier III data validation:**

C.1.b, C.1.c.i, C.1.c.ii, C.1.c.iv, C.1.c.v, C.1.vi, C.1.d.i, C.d.1.ii, C.1.d.iii, C.1.e, C.2.c.ii, C.2.c.iv, C.2.d.i, C.2.d.ii, C.2.d.iii, C.2.e

Table SV-XV-1:

QUALIFICATION OF SEMIVOLATILE ANALYTES BASED ON GPC CALIBRATION QUALITY CONTROL

	Criteria	Action
Peak Resolution	As per method QC acceptance criteria.	Professional Judgment
Peak Shape	Peak shapes must be symmetrical.	Professional Judgment
Retention Time Shift	Retention time shifts between GPC calibration checks must not exceed $\pm$ 5%.	Professional Judgment
GPC Instrument Blank	Target analytes must be < QL and surrogate compound recoveries and IS area counts and/or RTs (if added) must meet method QC acceptance criteria. (Note: CLP SOW OLM03.2 does not require the addition of surrogate compounds to the GPC instrument blank)	Refer to Section V for Blank Actions

Table VOA/SV-XI-2:

QUALIFICATION OF SEMIVOLATILE ANALYTES BASED ON GPC CLEANUP QUALITY CONTROL WHERE: # ONE-HALF OF GPC CALIBRATION CHECK COMPOUNDS OUTSIDE UPPER OR LOWER ACCEPTANCE LIMITS

Sample Results	% Recovery			
	%Rec < 10%	10% # %Rec < LL	LL # %Rec # UL	%Rec > UL
Detects	J	J	A	J
Non-detects	R	UJ	A	A

LL - Lower Limit of method QC acceptance criteria
UL - Upper Limit of method QC acceptance criteria

Table V/SV-XI-3:

QUALIFICATION OF SEMIVOLATILE ANALYTES BASED ON GPC CLEANUP QUALITY CONTROL WHERE: > ONE-HALF OF GPC CALIBRATION CHECK COMPOUNDS OUTSIDE UPPER OR LOWER ACCEPTANCE LIMITS

Sample Results	% Recovery			
	%Rec < 10%	10% # %Rec < LL	LL # %Rec # UL	%Rec > UL
All Detects	J	J	A	J
All Non-detects	R	UJ	A	A

Note: Professional judgment should be used when a combination of low recoveries and high recoveries are obtained.

LL - Lower Limit of method QC acceptance criteria
UL - Upper Limit of method QC acceptance criteria

Table SV-XV-4:

QUALIFICATION OF SEMIVOLATILE ANALYTES BASED ON SILICA GEL CLEANUP QUALITY CONTROL WHERE: # ONE HALF OF SILICA GEL CHECK SOLUTION COMPOUNDS OUTSIDE UPPER OR LOWER ACCEPTANCE CRITERIA

Sample Results	% Recovery			
	%Rec < 10%	10% # %Rec # LL	LL # %Rec # UL	%Rec > UL
Detects	J	J	A	J
Non-detects	R	UJ	A	A
Silica Gel Column Blank	Target analytes must be < QL and surrogate compound recoveries and IS area counts and/or RTs (if added) must meet method QC acceptance criteria.			Refer to Section V for Blank Actions

Note: Professional judgment should be used in applying the guidance above to qualify or reject sample data.

LL - Lower Limit of method QC acceptance criteria.
UL - Upper Limit of method QC acceptance criteria.

Table V/SV-XI-5:

QUALIFICATION OF SEMIVOLATILE ANALYTES BASED ON SILICA GEL CLEANUP QUALITY CONTROL WHERE: > ONE-HALF OF SILICA GEL CHECK SOLUTION COMPOUNDS OUTSIDE UPPER OR LOWER ACCEPTANCE LIMITS

Sample Results	% Recovery			
	%Rec < 10%	10% # %Rec < LL	LL # %Rec # UL	%Rec > UL
All Detects	J	J	A	J
All Non-detects	R	UJ	A	A

Note: Professional judgment should be used when a combination of low recoveries and high recoveries are obtained.

LL - Lower Limit of method QC acceptance criteria
UL - Upper Limit of method QC acceptance criteria

E. EXAMPLES

Example #1: (Unacceptable GPC peak resolution and retention time shift)

The validator compares the raw GPC calibration data with CLP SOW OLM03.2 criteria to verify that the proper collection and dump cycles were utilized to ensure that all interferences were removed without loss of target compounds. To do this, the validator reviews the peak shape, resolution, and retention time shift data for the GPC calibration. The validator notes that the calibration retention time shift exceeded the ± 5% criteria. The validator also notes that the baseline resolution between perylene and sulfur is less than 90%. The validator uses professional judgment to estimate (J) the positive detects and reject (R) the quantitation limits for non-detects for all samples associated with the non-compliant GPC calibration. The validator reports the qualified data on the Data Summary Table and discusses the low bias and potential false negatives due to insufficient column resolution and incorrect collect and dump cycles.

Example #2: (Silica Gel Check % recovery > upper limit for one compound)

The validator examines the raw Silica Gel cleanup data to verify that the percent recoveries from the Silica Gel Check meet method-specific QC acceptance criteria of 80-110%. The check solution contains several PAHs at 3 times the method quantitation limit. The validator notes that one of the check solution compounds, phenanthrene, was recovered at 150%. The validator uses professional judgment to estimate (J) the positive phenanthrene detects and accepts (A) the quantitation limits for phenanthrene non-detects on the Data Summary Table. The validator notes in the Data Validation Memorandum that a high bias exists for phenanthrene and that positive results of phenanthrene may actually be lower than the reported results.

XVI. SYSTEM PERFORMANCE

A. OBJECTIVE

The objective of assessing overall system performance is to determine if any method preparatory and/or analytical procedures result in qualitative and/or quantitative system error or bias. All sample, QC sample, and blank results are reviewed for accuracy, chromatography, precision, sensitivity, and contamination to ascertain if there are any general trends in data quality.

B. CRITERIA

Since there are no specific criteria for system performance, professional judgment should be used to assess the overall performance.

C. EVALUATION/ D. ACTION

C. EVALUATION	D. ACTION
*1. The results of Zero, Single and Double Blind PESs, MDL study, LFB, calibration standards, MS/MSD, and surrogate spike compound analyses may be used to assess the overall system accuracy including purge and extraction efficiency and instrument response. * a. Evaluate all PES and other relevant QC data to determine if any analytical trends exist over the sample analysis period. * b. The validator should ascertain from the PES and other relevant QC data if there is a high or low quantitative bias for a particular compound or group of compounds. * c. The validator should also ascertain from the PES and other relevant QC data if there is a potential for false negatives and/or false positives to be reported. * d. The validator should ascertain from the MS/MSD and surrogate spike compound analyses if the sample matrix effects impact compound recovery, thus indicating a method bias outside the control of the laboratory.	1. The validator should refer to the previous sections for specific guidance on evaluating accuracy using PES, MDL study, LFB, calibration standard, MS/MSD and surrogate data. If the validator determines that analytical trends indicate a qualitative and/or quantitative systematic bias, then the validator should use professional judgment to determine whether or not to qualify or reject the sample data based on the extent of the impact. The validator should discuss and justify all technical decisions in the Data Validation Memorandum. The validator should differentiate between sample matrix-related preparatory and analysis problems that are outside the laboratory's control and those preparatory and analysis problems that are within the laboratory's control.

C. EVALUATION	D. ACTION
*2. The results of the PES, LFB and calibration standard analyses as well as field samples may be used to assess the overall system chromatography. * a. Evaluate sample and QC sample reconstructed ion chromatograms analyzed on all columns to determine if the column chromatography, peak shape, resolution, and baseline drift has either deteriorated or improved over the sample analysis period. * b. The validator should ascertain from the raw data if unacceptable chromatography may contribute to a high or a low quantitative bias for a particular compound or group of compounds. * c. The validator should also ascertain from the raw data if unacceptable chromatography may result in a potential for false negative and/or false positive identifications. * d. The validator should determine if chromatography problems are a result of the sample matrix or are unique to the instrument. To that end, the validator should review the data package narrative for a discussion of possible matrix problems that the laboratory may have encountered. * e. The validator should determine if significant retention time shifts have occurred between initial and continuing calibration.	2. The validator should refer to the previous sections for specific guidance on evaluating compound identification and quantitation. If the validator determines that chromatographic trends indicate a qualitative and/or quantitative systematic bias, then professional judgment should be used to determine whether or not to qualify or reject the sample data based on the extent of the impact. The validator should discuss and justify all technical decisions in the Data Validation Memorandum. The validator should especially note when chromatography problems and column degradation are caused by severe matrix interferences. The validator should recommend additional cleanup procedures and/or alternate analytical methods for future site work.

C. EVALUATION	D. ACTION
*3. The results of the calibration standard, MDL study, internal standard, surrogate spike compound, MS/MSD, and field duplicate analyses may be used to assess overall system precision. * a. Compare the daily standard calibration area counts to ascertain if the instrument generated consistent detector responses over the sample analysis period. * b. Review the area counts of the internal standards and surrogate compounds for each sample to ascertain if there is a change in detector response. * c. The validator should evaluate the MS/MSD RPDs in conjunction with field duplicate RPDs to identify any analytical trends, ascertain if sample matrices were homogeneous or heterogeneous, and determine if sampling error may have contributed to field imprecision.	3. The validator should refer to the previous sections for specific guidance on evaluating laboratory and field precision and internal standard and surrogate compound analyses. If the validator determines that an instrument produces erratic detector responses, then they should use professional judgment to qualify or reject sample data. If MS/MSD RPDs indicate laboratory imprecision, then the validator should suspect laboratory technique and take into consideration the results of the field duplicate RPDs when using professional judgment to qualify sample data. If field duplicate RPDs indicate field imprecision resulting from heterogeneous sample matrices or field sampling error, then the validator should use professional judgment to qualify sample data based on the extent of impact. The validator should differentiate between lack of precision due to instrument performance problems and that caused by matrix effects or sampling error.

C. EVALUATION	D. ACTION
*4. The results of the LFB, PES, calibration and internal standard analyses may be used to assess the overall system sensitivity. (Note: VOA surrogates may also be used because they are equivalent to internal standards.) * a. Review all daily LFBs, low level calibration standards, and PES data to evaluate sensitivity for each instrument to verify that no instrument has lost its ability to accurately quantitate and identify compounds at the quantitation limit over the sample analysis period, which could potentially result in false negatives and low biased results. * b. Check the area counts of the individual sample, QC sample, calibration and blank internal standards and calibration standards to monitor instrument sensitivity changes. * c. Review the sample chromatograms for abrupt, discrete shifts in the chromatographic baseline which may indicate a change in the instrument's sensitivity or the zero setting. A baseline "decline" could indicate a decrease in sensitivity in the instrument or an increase in the instrument zero, possibly causing target compounds, at or near the detection limit, to miss detection (false negatives). Additionally, a decline in the baseline may result in incorrect peak integration and subsequent misquantitation. A sudden baseline shift could indicate problems such as a change in the instrument zero, a leak, degradation of the column or the formation of matrix degradation products.	4. The validator should refer to the previous sections for specific guidance on evaluating sensitivity, accuracy, compound identification, and quantitation. If the validator determines that instrument sensitivity is unacceptable, then the validator should use professional judgment to qualify or reject the affected sample data. The validator should discuss and justify all technical decisions in the Data Validation Memorandum. The validator should also note if sample matrix interferences did not allow quantitation limits to be achieved and should recommend additional cleanup procedures and/or alternate analytical methods for future site work.

C. EVALUATION	D. ACTION
*5. The results of the PES and method, instrument, cleanup, equipment/rinsate, trip, storage and bottle blank analyses may be used to assess overall system contamination. * a. Review all blank and sample results to evaluate the possibility of sample contamination introduced via either cross- contamination from a previously run sample or from general lab contamination. * b. Compare blank analysis on two different instruments to determine if the contamination is instrument related or the interferents are present in the blank from sample processing activities. * c. Assess whether problematic blank results are reproducible when replicate aliquots are analyzed or are sporadic interferences. Sporadic interferences, such as methylene chloride, acetone or phthalates, may indicate that the interferent is introduced from the laboratory environment. The validator should review sample chromatograms for suspected outlier interferents.	5. The validator should refer to the previous sections for specific guidance on evaluating blank contamination. If the validator determines that there is a systematic blank error introduced during sample collection or processing (extraction or analysis), then the data should be qualified according to Section V. However, if the validator suspects intermittent or sporadic introduction of interferents during analysis, then the validator should use professional judgment to qualify or reject sample data and document and justify all technical decisions in the Data Validation Memorandum.

*** Note: This section is only applicable to a Tier III data validation - If a validator suspects system performance has degraded to the degree that data are affected and a Tier II validation has been requested, then the validator should contact the Site Manager to approve the necessary Tier III validation.**

E. EXAMPLES

Example #1: (Abrupt decrease in baseline)

The validator notices a significant abrupt decrease in the baseline during the analysis of aqueous sample SAP55. The validator examines the IS area counts and observes that a decrease in the area counts for the last two internal standards has occurred. The validator notes that the VOA surrogate compound areas for the last two surrogates also decreased. There were no PE samples associated with these samples available for review. The validator uses professional judgment to estimate (J) all positive detects associated with the two problematic internal standards and rejects (R) all non-detects associated with the two problematic internal standards. The validator reports the qualified data on the Data Summary Table. The validator notes the sensitivity loss of the GC/MS instrument and justifies the decision to qualify sample data in the Data Validation Memorandum.

Example #2: (Peak broadening and tailing for volatile gases; PES quantitation low for 1 volatile gas)

The validator reexamines the Reconstructed Ion Chromatograms from packed column analysis and notices peak broadening and tailing of the following volatile gases: vinyl chloride, chloromethane, bromoethane, and chloroethane. The PE sample results were reviewed and found to have an "Action Low" qualification for vinyl chloride which was the only volatile gas included in the PES. The validator uses professional judgment to estimate (J) all positive volatile gas detects in all samples associated with that PES, and to estimate (UJ) the quantitation limits for all volatile gas non-detects in all samples associated with that PES. The validator reports the qualified data on the Data Summary Table. The validator notes the GC/MS chromatography problem and justifies the decision to qualify sample data in the Data Validation Memorandum.

XVII. OVERALL EVALUATION OF DATA

A. OBJECTIVE

The objective of the final evaluation of a data package is to identify the "analytical error" and any "sampling error" associated with the data. The sum of the "analytical error" and the "sampling error" equals the "measurement error". "Measurement error" will then be used by the end user in conjunction with sampling variability (spatial variations in pollutant concentrations) to determine "total error" (total uncertainty) associated with the data. Ultimately, the end data user will assess data usability in the context of the pre-determined Data Quality Objectives (DQOs) and resultant "total error" of the data.

B. CRITERIA

The Sampling and Analysis Plan (SAP) or Quality Assurance Project Plan (QAPjP) and DQO Summary Form should specify the site specific DQOs and acceptable levels of uncertainty or "total error".

C. EVALUATION/ D. ACTION

C. EVALUATION	D. ACTION
1. Obtain the SAP, QAPjP or DQO Summary Form to review the DQOs for the sampling event.	1. Synopsize in the first section of the Data Validation Memorandum, Overall Evaluation of Data, in bullet format, the appropriate project DQOs for the data package.
2. Evaluate the appropriateness of the analytical method chosen. For example, was the method capable of achieving quantitation limits sufficiently low to meet DQOs for risk assessment? Was the method capable of successfully analyzing each particular matrix sampled?	2. If an inappropriate method was chosen for sample analysis, then the validator should discuss the method deficiencies and identify more appropriate methods or modifications for use in subsequent sampling rounds. The validator should include this discussion in the Overall Evaluation of Data Section of the Data Validation Memorandum.

C. EVALUATION	D. ACTION
3. Evaluate any analytical problems that were identified.	3. Estimate and describe the "analytical error" that contributes to the "measurement error" associated with the data package in the Overall Evaluation of Data Section of the Data Validation Memorandum. a. If "analytical error" causes the data to be unusable, then the validator should reject the data and return it to the laboratory and deny payment. b. If "analytical error" causes the data to be of reduced worth to the Region, then the validator should recommend that the laboratory's payment be reduced.
4. Evaluate any sampling issues that were identified. Note: The validator is only responsible for evaluating those "sampling errors" that are identified during the routine data validation process. Other "sampling errors" may have occurred and they should be assessed by the end user prior to data use.	4. Estimate and describe the "sampling error" that contributes to the "measurement error" associated with the data package in the Overall Evaluation of Data Section of the Data Validation Memorandum. Examples of "sampling error" for which the validator would have information include highly contaminated trip or equipment blanks as well as delayed sample shipment that caused holding time violations. a. If "sampling error" severely impacts potential data usability, then the validator should note this in the Data Validation Memorandum. b. The end user should review the results of the sampler's field notes/trip report to determine additional "sampling error" issues with which to fully assess "measurement error".

C. EVALUATION	D. ACTION
5. Evaluate data quality in terms of "measurement error" as a combination of "analytical error" and "sampling error".	5. Discuss data quality in terms of "measurement error" as the sum of "analytical error" and "sampling error". All discussions should be included in the Overall Evaluation of Data Section of the Data Validation Memorandum.
6. Identify potential usability issues raised by an unacceptable degree of "measurement error".	6. If data usability is potentially compromised by a high degree of "measurement error", then the validator should note this in the Overall Evaluation of Data section of the Data Validation Memorandum. If data quality impacts the use of those data by the end user, then the validator should detail in the Overall Evaluation of Data Section of the Data Validation Memorandum how data use will be limited and for which end user, i.e., risk assessor, hydrogeologist, etc..
7. Sampling variability is not assessed during data validation, and therefore, should be assessed by the end user prior to data use.	7. The end user should review the results of the Data Validation Memorandum in conjunction with the sampler's field notes/trip report to assess the impact of sampling variability issues on data usability.